Aluminum in Acidic Surface Waters: Chemistry, Transport, and Effects

by Charles T. Driscoll*

Ecologically significant concentrations of Al have been reported in surface waters draining "acid-sensitive" watersheds that are receiving elevated inputs of acidic deposition. It has been hypothesized that mineral acids from atmospheric deposition have remobilized Al previously precipitated within the soil during soil development. This Al is then thought to be transported to adjacent surface waters.

Dissolved mononuclear Al occurs as aquo Al, as well as OH^-, F^-, SO_4^{2-}, and organic complexes. Although past investigations have often ignored non-hydroxide complexes of Al, it appears that organic and F complexes are the predominant forms of Al in dilute (low ionic strength) acidic surface waters. The concentration of inorganic forms of Al increases exponentially with decreases in solution pH. This response is similar to the theoretical pH dependent solubility of Al mineral phases. The concentration of organic forms of Al, however, is strongly correlated with variations in organic carbon concentration of surface waters rather than pH.

Elevated concentrations of Al in dilute acidic waters are of interest because: Al is an important pH buffer; Al may influence the cycling of important elements like P, organic carbon, and trace metals; and Al is potentially toxic to aquatic organisms. An understanding of the aqueous speciation of Al is essential for an evaluation of these processes.

Introduction

Aluminum is an abundant element within the lithosphere (1). It occurs primarily in aluminosilicate minerals, most commonly as feldspars in metamorphic and igneous rocks and as clay minerals in well-weathered soils. In high elevation, northern temperate regions, the soils encountered are generally spodosols (2). In these regions, the process of soil development is thought to involve the mobilization of Al (and Fe) from upper to lower mineral soil horizons by organic acids leached from foliage as well as from decomposition in the forest floor (3–6). As alumino-organic complexes are transported through the mineral soil, processes of complexation and/or microbial oxidation result in a decrease in the organic carbon to Al ratio and a reduction in the solubility of these solutes (7–9). In pristine environments Al appears to be largely retained within the lower (B horizon) soil. Ugolini et al. (9) reported that there was little transport of Al from soil to surface water associated with soil developmnet at Findley Lake in Washington.

The concentrations of dissolved Al are generally low in most circumneutral waters due to the relatively low solubility of natural Al minerals. Stumm and Morgan (10) report a median value of 0.4 µmole/L for terrestrial waters, while Bowen (11) gives an average concentration of 9 µmole/L for freshwaters including bogs.

Superimposed on the natural process of soil development in northern forested ecosystems is the introduction of mineral acids from atmospheric deposition. High elevation watersheds with soils that are highly permeable, underlain by silicate bedrock, shallow, and acidic (low in exchangeable basic cations: Ca^{2+}, Mg^{2+}, Na^+, K^+) are generally sensitive to atmospheric deposition of mineral acids. The input and subsequent transport of conservative anions (e.g., SO_4^{2-}) through an ecosystem will result, by electroneutrality, in an equivalent flux of cations. Because pools of readily available basic cations are low, inputs of conservative anions may not be entirely compensated by the release of basic cations from "acid-sensitive" watersheds. As a result, acidic cations (H^+, Al^+) may be transported with conservative anions from soil to surface waters. Cronan and Schofield (12) have hypothesized that mineral acids from atmospheric deposition have altered the natural process of soil development in northern temperature soils by facilitating the transport of Al from soil to surface waters. Evidence to support this contention is available through water chemistry data collected from "acid-sensitive" regions that are receiving high atmospheric loading of strong acids. When the equivalence of acidic anions (e.g., SO_4^{2-}, NO_3^-) approaches or exceeds the equivalence of basic cations, high concentrations of acidic cations (H^+, Al''^+) are observed in surface waters (Fig. 1). Elevated concentrations of Al have been reported in acidic waters within regions receiving high inputs of acidic substances, such as Sweden (13), Nor-

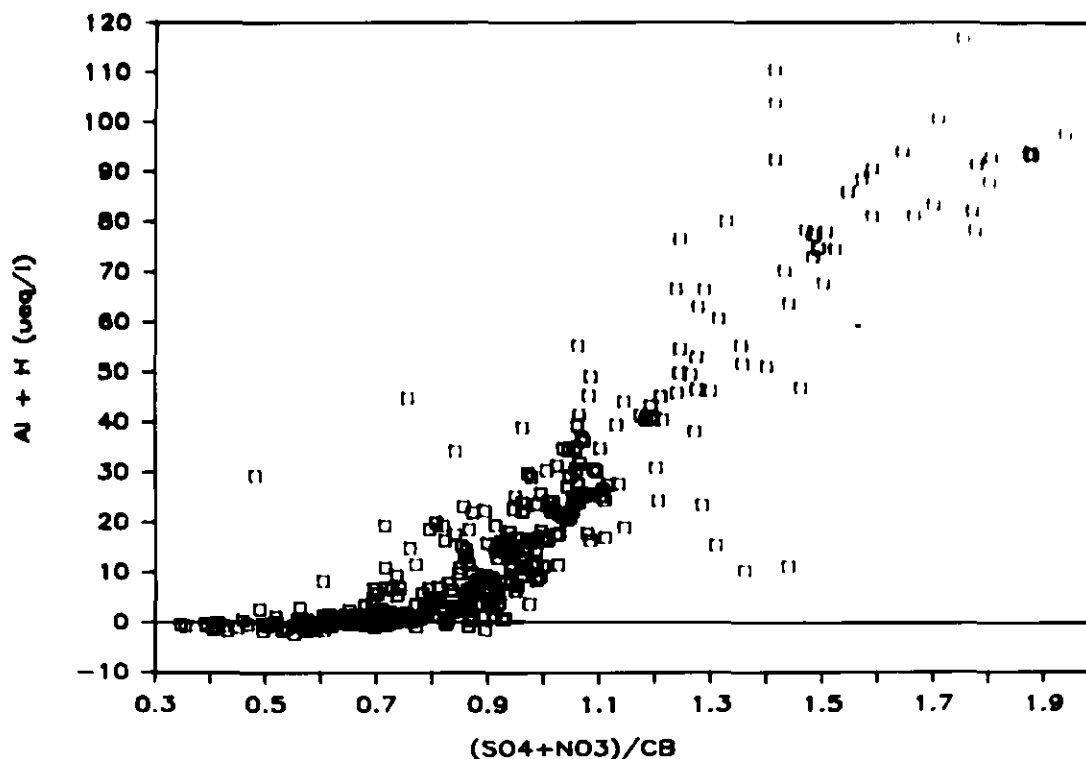*Department of Civil Engineering, Syracuse University, Syracuse, NY 13210.

FIGURE 1. Equivalence of acidic cations (H^+, Al''^-) as a function of the ratio of SO_4^{2-} and NO_3^- equivalence to basic cation equivalence (C_B, Ca^{2+}, Mg^{2+}, Na^+, K^+) for Adirondack surface waters. As the equivalence to basic cation equivalence approaches one, significant increases in the concentrations of acidic cations (H^+, Al''^+) are observed. The equivalence of Al is computed by considering the various inorganic complexes.

way (14), Belgium (15), the Netherlands (16), Germany (17), Ontario, Canada (18), and the northeastern United States (12).

Distribution and Sources of Aluminum

Dissolved monomeric Al occurs as aquo Al as well as OH^-, F^-, SO_4^{2-} and organic complexes (19,20). A number of fractionation procedures have been developed in recent years to attempt to distinguish between aqueous forms of Al. These techniques include dialysis (21), batch cation exchange (22), column cation exchange (23), F ion-selective electrode (23), and morin addition followed by fluorimetric detection (24). All these procedures are operationally defined and undoubtedly detect somewhat different forms of Al.

Driscoll and co-workers (23,25–27) have used a column cation-exchange procedure to fractionate the Al in surface waters of the Adirondack region of New York State and New Hampshire into labile monomeric Al, nonlabile monomeric Al, and acid-soluble Al (Fig. 2). Labile monomeric Al is thought to represent aquo Al as well as inorganic complexes of Al (e.g., OH^-, F^-, SO_4^{2-}). Nonlabile monomeric Al is thought to

represent organic complexes of Al, while acid-soluble Al is considered to be colloidal Al and/or very strong alumino-organic solutes. Results of these studies have indicated that concentrations of labile monomeric Al increased exponentially with decreases in solution pH (Fig. 3). Concentrations of nonlabile monomeric Al were strongly correlated with organic carbon concentration in both Adirondack ($Al_0 = -3.26 \times 10^{-6} + 0.0204$ TOC, where Al_0 is nonlabile, monomeric aluminum in μmole/L and TOC is total organic carbon concentration in μmole C/L, $n = 322$, $r^2 = 0.76$, $p < 0.0001$) (Fig. 4), and New Hampshire ($Al_0 = -7.3 \times 10^{-7} + 0.0155$ DOC; where DOC is the dissolved organic carbon concentration in μmole C/L, $n = 69$, $r^2 = 0.85$, $p < 0.0001$) surface waters (23).

Using the column ion exchange fraction procedure, Driscoll et al. (26) observed that labile monomeric Al was the predominant form of Al in acidic Adirondack surface waters, although concentrations of nonlabile monomeric Al were also significant (Table 1). These authors applied values of labile monomeric Al, pH, F^-, and SO_4^{2-} to a chemical equilibrium model to calculate the distribution of inorganic Al (23). Fluoride-complexed Al was the predominant form of labile monomeric Al in acidic surface waters, and at pH values below 5.5 essentially all aqueous F was complexed with Al. Concentrations of aquo Al and OH-complexed Al were less significant than F-complexed-Al. Sulfate complexes of
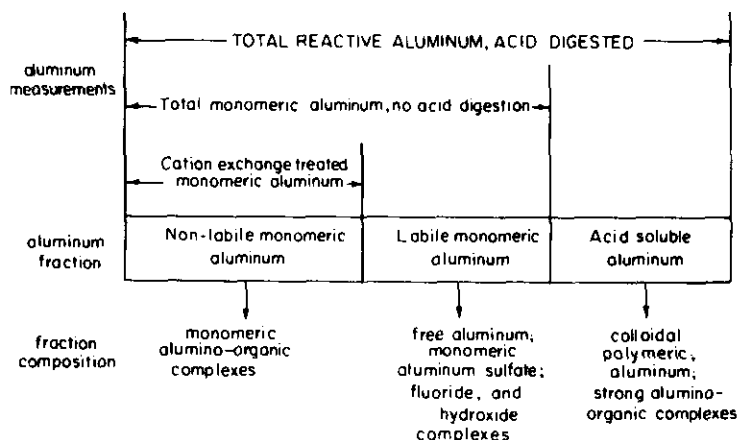
FIGURE 2. Schematic diagram of the procedure for the fractionation of aqueous Al proposed by Driscoll (23). Three Al measurements are made in this procedure, total Al (acid digestion), total monomeric Al (addition of a complexing agent followed by rapid extraction into an organic solvent), and nonlabile monomeric Al (separation through a cation exchange column followed by analysis as monomeric Al). From these three measurements, three Al fractions are determined. Nonlabile monomeric Al is measured directly and thought to be an estimate of Al that is complexed with organic matter. Labile monomeric Al is determined as the difference between monomeric and nonlabile monomeric Al, and includes aquo Al as well as OH^-, F^-, SO_4^{2-} complexes of Al. Acid-soluble Al is total Al less total monomeric Al and is an estimate of those forms of Al that require acid digestion for detection. This latter fraction would include colloidal Al and very strongly bound alumino-organic forms.

Al were small in magnitude.

Many investigators have observed an exponential increase in Al concentration with decreasing solution pH (13,15,26,28,29). This phenomenon is characteristic of the theoretical and experimental solubility of a number of Al minerals. In order to better understand the Al cycle and to develop predictive models to assess the effects of acidic deposition, it is critical to identify the source of mobile Al. Researchers have hypothesized several mechanisms for the solid phase controlling Al concentrations in dilute water systems, including poorly crystallized 1:1 layer clays (30), kaolinite (31), $Al(OH)_3$ (27), jurbanite (32), and dissociation from soil organic matter (33).

Johnson et al. (27) and Driscoll et al. (26) evaluated the chemistry of surface waters in New Hampshire and in the Adirondack region of New York, respectively,

and reported that solutions were generally similar to the solubility of $Al(OH)_3$ (Fig. 5). Driscoll et al. (26) reported that under high flow conditions and when solutions contained high concentrations of TOC, the ion activity product of Adirondack solutions were undersaturated with respect to Al $(OH)_3$ solubility. This observation suggests that the retention time of water in the soil and/or the flow paths of water through organic and mineral soil may be important processes regulating stream concentrations of Al.

In acid-sensitive regions of Europe, a number of investigators have reported that the activity of aquo Al in groundwaters (32) and soil solutions (34) appears to be regulated by the solubility of jurbanite [$Al(OH)SO_4 \cdot 5H_2O$]. The apparent discrepancy between phases regulating the solubility of Al in Europe and North America may be attributed to differences in solution chemistry. In acid-sensitive regions of North America (e.g., Adirondacks, New England) the pH values are generally greater than 4.2 and the SO_4 concentrations range from 100 to 200 μeq/L. Under these conditions, solutions are highly undersaturated with respect to the solubility of $Al-SO_4$ minerals (26). However, in Europe, solution concentrations of sulfate are considerably greater and pH values are lower than observed in Eastern North America (35). High loadings of H_2SO_4 have resulted in extreme acidification, producing conditions that are conclusive to the formation of $Al-SO_4$ minerals (36). Unfortunately the identification of a mineral phase that regulates aqueous Al by thermochemical calculations is tenuous. Results will vary considerably, depending on the source of thermochemical data and whether the researcher includes ionic strength, and temperature corrections or complexing ligands (e.g., F^-, DOC) in these calculations.

Additional information on processes regulating aqueous concentrations of Al is available through soil solution and soil chemistry data. Studies of soil solution and soil Al from the Adirondack region of New York (37) and New Hampshire (38) have yielded comparable results. Solutions draining the forest floor contained remarkably high concentrations of Al, which appeared to be largely associated with organic matter. These solutions were highly undersaturated with respect to the solubility of readily forming mineral phases. In the lower mineral soil (B horizon), concentrations of inorganic Al were elevated and solutions approached the

Table 1. Distribution of aqueous aluminum in Adirondack surface water (n = 321).[a]

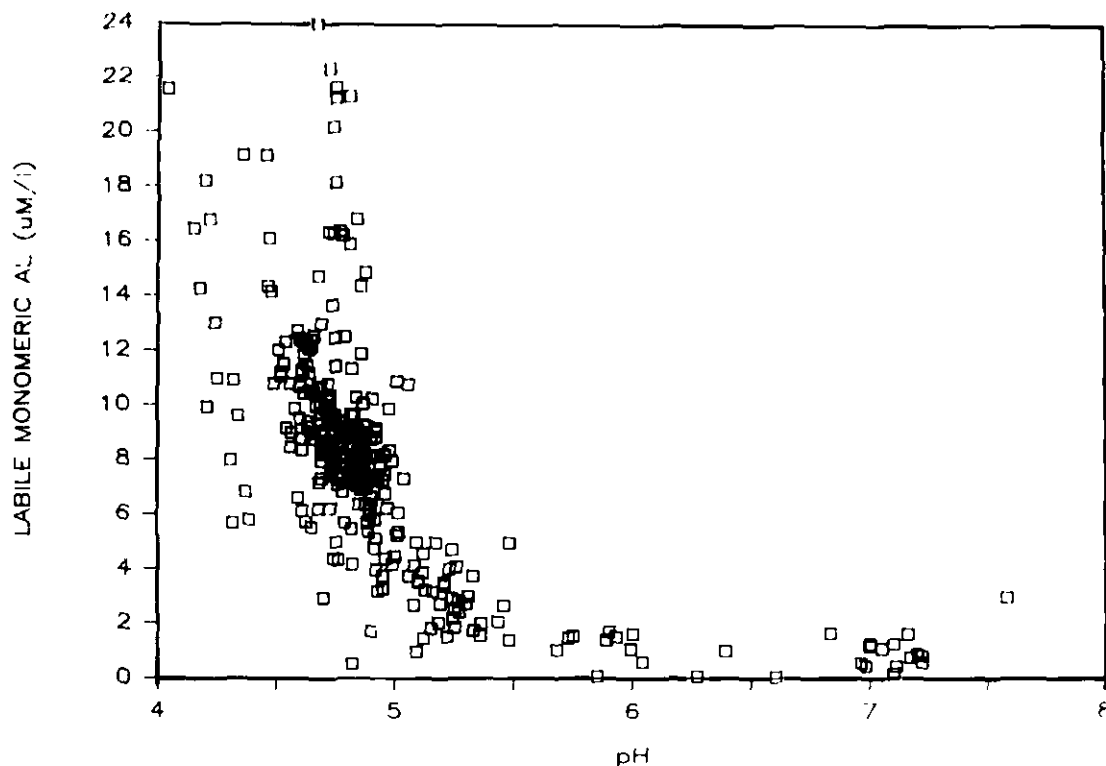| Aluminum form	Aluminum concentration ($\pm$ Std. dev.), μmole/L	Aluminum distribution Total	Aluminum distribution As monomer
Total	16.1 $\pm$ 6.9	—	—
Labile monomeric	7.7 $\pm$ 4.7	0.48	0.56
Nonlabile monomeric	6.2 $\pm$ 4.1	0.37	0.44
Acid-soluble	2.1 $\pm$ 1.8	0.14	—
Aquo	1.6 $\pm$ 1.3	0.10	0.11
Hydroxide complexed	1.9 $\pm$ 1.9	0.25	0.14
Fluoride complexed	4.0 $\pm$ 1.9	0.25	0.29
Sulfate complexed	0.2 $\pm$ 0.2	0.01	0.01

[a] Data of Driscoll (26).

FIGURE 3. Concentrations of labile monomeric Al as a function of pH in Adirondack surface waters (24).

solubility of $Al(OH)_3$ (natural gibbsite, $p*K_{so} = 8.77$) (39). The analysis of free Al fractions in soil [1.0 M KCl, exchangeable; 0.1 M $Na_4P_2O_7$, organic; 0.2 M $(NH_4)_2C_2O_4$ adjusted to pH 2, amorphous; citrate-di-thionite-bicarbonate, crystalline free] (40) in these studies suggested that much of this Al is extractable in pyrophosphate and therefore thought to be associated with organic matter. However, chemical extraction techniques are not specific and should be interpreted with caution (41).

Results of these field studies in the northeastern U.S. (37,38) led the investigators to conclude that the forest floor was a significant source of mobile Al. The Al transported from the organic horizons was largely in an organic form and probably the by-product of decomposition processes. These observations are to some extent inconsistent with the traditional views of soil development and suggest that biocycling (vegetation assimilation and microbial decomposition) is an important component of the Al cycle in forest ecosystems in the northeastern U.S. Elevated concentrations of inorganic Al were generally observed only in B horizon solutions. Therefore, it is likely that organic and inorganic fractions of Al observed in surface waters originate from different processes (decomposition and dissolution, respectively) and at different locations within the soil profile (O and B horizons, respectively).

Very little useful information has been obtained from X-ray diffractometer tracing on soil samples. However, April and Newton (42) have observed vermiculite, chloritized with $Al(OH)_3$, in Adirondack soils. Although there

is very little data on the solubility of interlayer $Al(OH)_3$, this observation may be consistent with the solubility of Al reported for Adirondack surface waters (26) (Fig. 5).

It is apparent that there are inconsistencies in the literature on the process regulating aqueous aluminum concentration in dilute acidic waters. If we intend to upgrade the models that have been developed to assess the extent and effects of surface water acidification (43) it is essential that we develop a better understanding of the mechanisms of aluminum mobilization.

Temporal and Spatial Variations in Aqueous Aluminum

Pronounced temporal and spatial variations in the concentration of aqueous Al have been reported for acidic surface waters. Schofield and Trojnar (44) observed low pH and high Al concentrations in an Adirondack stream during hydrologic events, particularly snowmelt. Driscoll et al. (25) also observed this phenomenon but attributed these increases to the labile (inorganic) form of monomeric Al. During low flow conditions, pH values were circumneutral (pH 5.5–7.0), presumably due to the increased retention time of water in the mineral soil, and labile monomeric Al concentrations were low in Adirondack streams. Through the summer and on into the autumn, the organic carbon and nonlabile monomeric Al concentrations increased. During winter and spring the concentration of both these
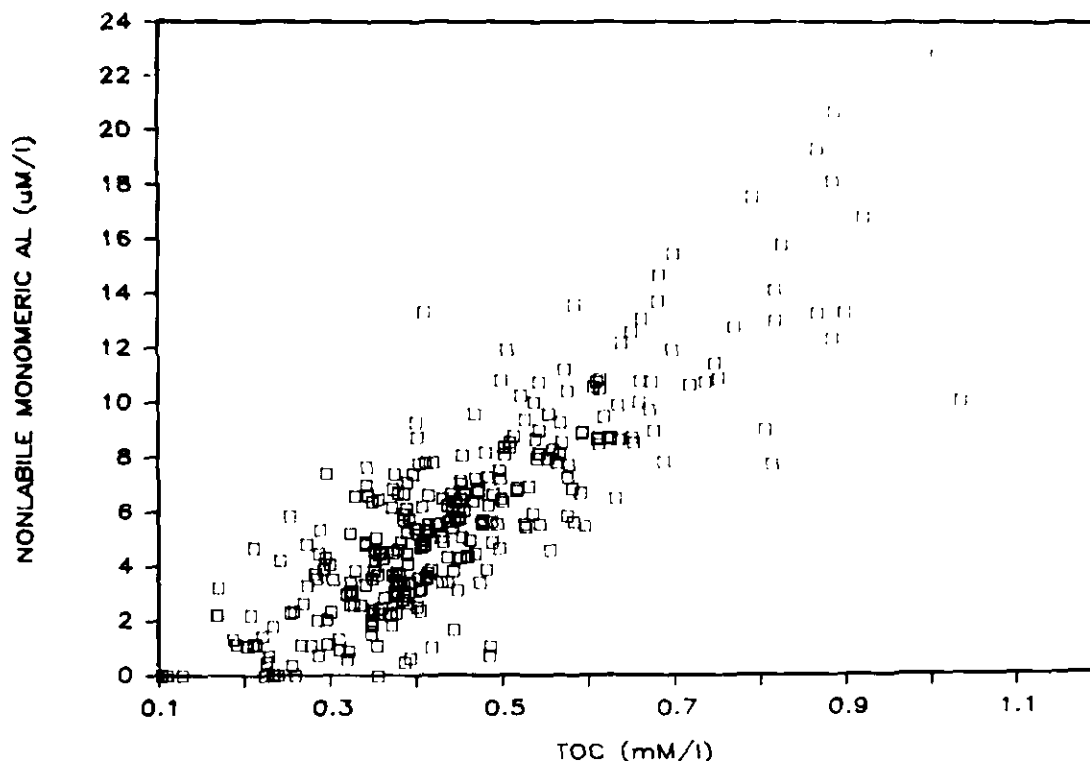
FIGURE 4. Concentrations of nonlabile monomeric Al as a function of total organic carbon concentration (mmole C/L) in Adirondack surface waters (24).

parameters were relatively low on the Adirondack streams.

The nature of these short-term changes in H^+ and Al can best be illustrated with a soluble equivalence diagram (Fig. 6). Pulsed inputs of NO_3^- are typically observed during snowmelt in "acid-sensitive" watersheds in the northeastern U.S. (45). Because these catchments have low pools of "readily-available" basic cations, NO_3^- inputs are generally accompanied by a stoichiometric increase in acidic cation (H^+, Al^{n+}) equivalence. While the pulsed inputs of SO_4^{2-} have been observed in Scandinavia (46), the additional acidity observed in surface waters during snowmelt in the northeastern U.S. can almost exclusively be attributed to NO_3^- increases. Although this NO_3^- acidity is clearly an important factor contributing to the short-term acidification of surface waters, its source is uncertain. Johannes et al. (47) reported that NO_3^- storage in snowpack from the Adirondack region was greater than SO_4^{2-}. Also the oxidation of organic N from the forest floor and subsequent transport during snowmelt may also contribute to HNO_3 acidification.

Johnson et al. (27) studied the temporal and spatial variations of a headwater stream system in New Hampshire. Temporal variations in Al chemistry were similar to those reported for the Adirondacks (26,43). Johnson et al. (27) also reported decreases in H^+ (pH increases) and Al and increased concentrations of basic cations, with increasing stream order (and drainage area). They suggested a two-step process for the neutralization of

acidic deposition. Mineral acidity entering the ecosystem from atmospheric deposition was converted to a mixture of H^+ and Al base-neutralizing capacity (BNC; acidity) in headwater streams and was subsequently neutralized by the dissolution of basic cations from the mineral soil.

Johnson et al. (27) also observed a shift in Al speciation with increasing stream order. Aquo Al and OH complexed Al concentrations decreased substantially with increasing drainage area. Aluminofluoride complexes remained constant throughout the experimental reach, while nonlabile Al concentrations increased with decreasing elevation.

Driscoll and Schafran (45) have evaluated the temporal and spatial variations in the Al chemistry and BNC of an acidic Adirondack Lake, Darts Lake. They defined H-Al-BNC (hydrogen ion, aluminum base-neutralizing capacity) as the amount of strong base required to increase the pH of a liter of Al solution to 8.3. Variations in H-Al-BNC were strongly correlated with variations in NO_3^- concentration (H-Al-BNC = 2.4 + 0.94 NO_3^-; $\mu eq/L$, $n = 172$, $r^2 = 0.54$, $p < 0.0001$). Note that this empirical correlation is linear with a slope close to one and an intercept near the origin. Although SO_4^{2-} was the dominant anion in Darts Lake solutions, no statistically significant relationship with H-Al-BNC was observed. H-Al-BNC was negatively correlated with organic anion concentrations (H-Al-BNC = 222 − 16 $RCOO^-$; where $RCOO^-$ represents the organic anion concentration in $\mu eq/L$, $n = 172$, $r^2 = 0.45$, $p < 0.0001$)
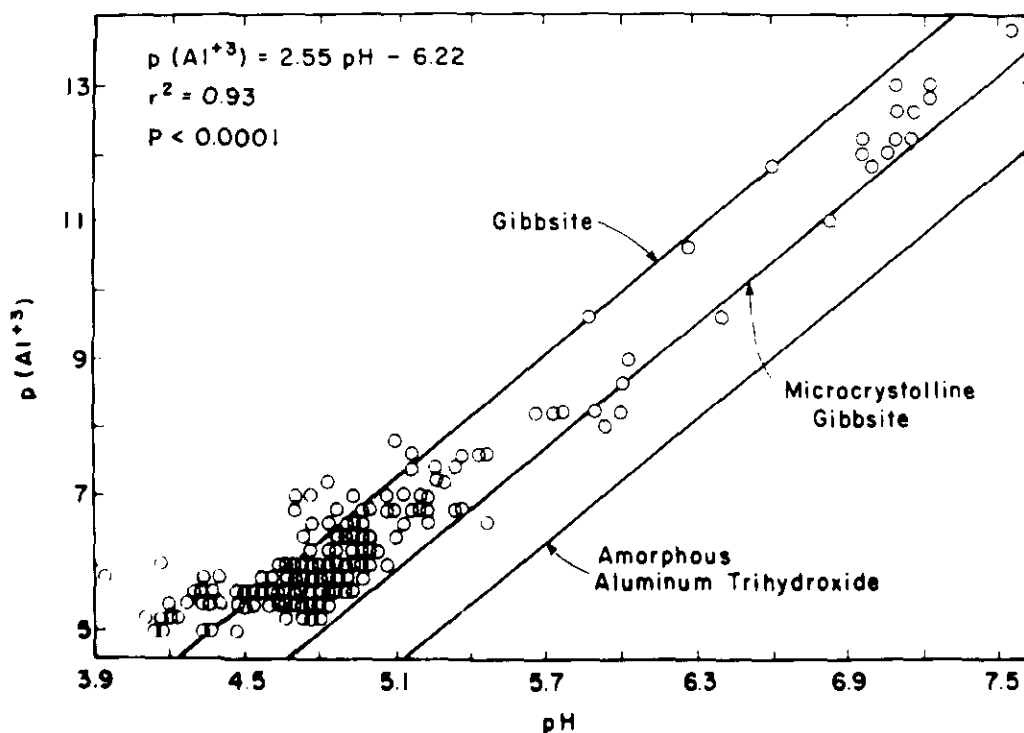
FIGURE 5.   The activity of aquo Al as a function of pH in Adirondack surface waters (24). The activity of Al^{3+} was calculated from measurements of labile monomeric Al, pH, F^-, and SO_4^{2-} using a chemical equilibrium model.

and no statistically significant relationship was observed with Cl.

Driscoll and Schafran (45) suggested that ecosystem processes cause temporal and spatial variations in NO_3^- which influence H-Al-BNC. During spring, snowmelt resulted in large inputs of water containing elevated concentrations of NO_3^- and H-Al-BNC to Darts Lake. From mass balance calculations, Driscoll and Schafran (48) observed that during the snowmelt period essentially all of the Al that entered Darts Lake at the inlet stream was transported out the outlet (Table 2). The conservative nature of Al within the lake, during the snowmelt period, was further illustrated by mineral saturation index calculations (SI) (Fig. 7):

$$SI = \log Q_p/K_p$$

where Q_p is the ion activity product of the solution and K_p is the thermodynamic solubility of the mineral phase of interest. An SI value of greater than zero suggests that the solution is oversaturated with respect to the solubility of the mineral phase of interest. An SI value near zero suggests equilibrium and a negative value indicates undersaturation.

During the high flow conditions associated with snowmelt, Darts Lake solutions were highly undersaturated with respect to readily forming mineral phases (microcrystalline gibbsite, $p^*K_{so} = 9.35$) (49) (Fig. 7). These calculations suggest that in-lake formation of particulate Al was not favored thermodynamically and probably did not occur to any extent during snowmelt. Conditions of

undersaturation may be attributed to relatively slow dissolution kinetics of Al minerals and/or minimal contact of solutions with the mineral soil due to the short-circuiting of water from the forest floor directly to the stream.

During the summer stratification period, NO_3^- concentrations in the water column were reduced through a combination of lower inlet concentrations, algal assimulation of NO_3^-, and denitrification. Retention of NO_3^- by these latter two processes resulted in the production of acid neutralizing capacity within the lake and a water column that was oversaturated with respect to the solubility of microcrystalline gibbsite (Fig. 7). Positive SI values suggest in-lake formation of particulate Al, and mass flux calculations confirm that considerable Al was retained in the lake during the summer stratification period (Table 2).

An often overlooked but potentially important mechanism of Al transport is the dissociation of $H_2CO_3^*$ (50). Within soil and hypolimnitic environments, microbial respiration results in solutions that are highly oversaturated with respect to the solubility of atmospheric CO_2 ($10^{-3.5}$ atm). The dissociation of $H_2CO_3^*$, at high partial pressures of CO_2, produces concentrations of H^+ capable of solubilizing particulate Al, and the formation of HCO_3^- which may serve as a mobile anion and facilitate the transport of this Al. However, when these solutions are exposed to the atmospheric conditions (e.g., soil solutions transported to surface waters or turnover occurs in lakes) CO_2 will degas, resulting in an increase in solution pH, the removal of HCO_3^-, and
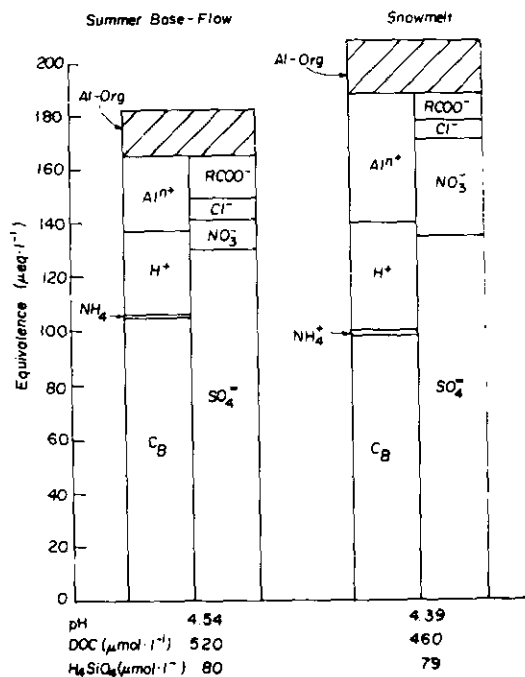
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FIGURE 7. Isopleth of the saturation index (SI) of Darts Lake water with respect to the solubility of microcrystalline gibbsite ($p*K_{so}$ = 9.35) (49). Note that during spring high flow conditions, the lake water was highly undersaturated with respect to the solubility of microcrystalline gibbsite and Al conservative within the lake system. During periods of stratification in-lake retention of NO_3^- resulted in increases in solution pH and highly positive values of SI. These calculations suggest that in-lake formation of particulate Al was favored during stratification.

FIGURE 6. Equivalence distribution of solutes in an Adirondack lake (Merriam Pond) under spring high flow (February, March, April; 8 observations) and summer base flow (June, July, August, September; 10 observations) conditions. C_B is the sum of the basic cation equivalence (Ca^{2+}, Mg^{2+}, Na^+, K^+). The equivalence of inorganic Al (Al^{n+}) is calculated by considering the various inorganic complexes. Organic Al (Org Al) is assumed to be trivalent and balanced by an equivalent organic ligand. Free organic anions ($RCOO^-$) are calculated as the difference between inorganic cations and inorganic anions.

the hydrolysis of Al. The conditions and extent to which this process may occur are illustrated in Figure 8 for Darts Lake. Carbon dioxide retained Al is defined as that quantity of Al held in solution by CO_2 that is oversaturated with respect to the solubility of atmospheric CO_2, assuming that the solubility of Al is controlled by microcrystalline gibbsite (49). Note that, while concentrations of Al were highest at low acid-neutralizing capacity (ANC) and pH values, the partial pressure of CO_2 was not adequate to produce significant concentrations of HCO_3^-. As ANC values increased, HCO_3^- concentrations increase but the solubility of Al decreases. Because concentrations of HCO_3^- and Al are pH-de-
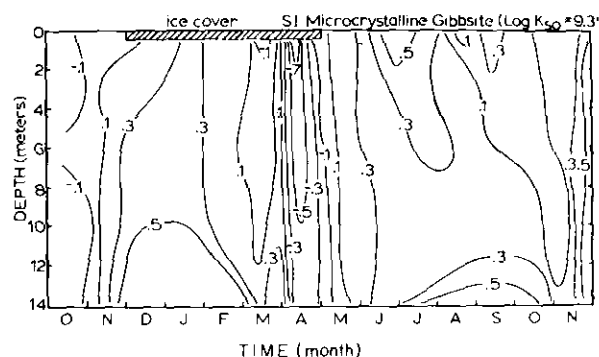
pendent, maximum concentrations of CO_2-retained Al occurred near ANC values of zero and pH values near 5. Darts Lake contains up to $10^{-2.4}$ atm of CO_2 in the lower waters during periods of stratification and has been observed to have as much as 8 μmole/L CO_2-retained Al.

Particulate Al formed by CO_2 degassing or NO_3^- reduction is undoubtedly deposited on stream and lake sediments. These pools of Al may be readily resolubilized during episodic events (50,51).

Effects of Aluminum in Acidic Surface Waters

Aluminum as a pH Buffer

Dilute water systems are characteristically low in dissolved inorganic carbon (DIC) due to the limited dissolution of soil minerals. Because dilute waters are inherently low in DIC, they are limited with respect to inorganic carbon buffering capacity. Consequently, noninorganic carbon acid/base reactions, such as hydrolysis of Al and protonation/deprotonation of natural organic carbon, may be important in the pH buffering of dilute waters.

Several researchers have investigated noninorganic carbon, weak acid/base systems in dilute waters. Dickson (13) observed that elevated concentrations of Al increased the BNC of Swedish lakes. Waters were strongly buffered by Al in the pH range 4.5 to 5.5. The BNC of Al was particularly evident when acidic lakes were treated with base (limed). Aluminum BNC was comparable in magnitude to H^+ and inorganic carbon BNC; therefore, the presence of Al substantially increased base dose requirements and the cost associated with the renovation of acidic lakes.

Johannessen (52) investigated nonhydrogen ion/inorganic carbon buffering in Norwegian waters. While

Table 2. Mass flux of total aluminum in, out and retained in the sediments of Darts Lake.

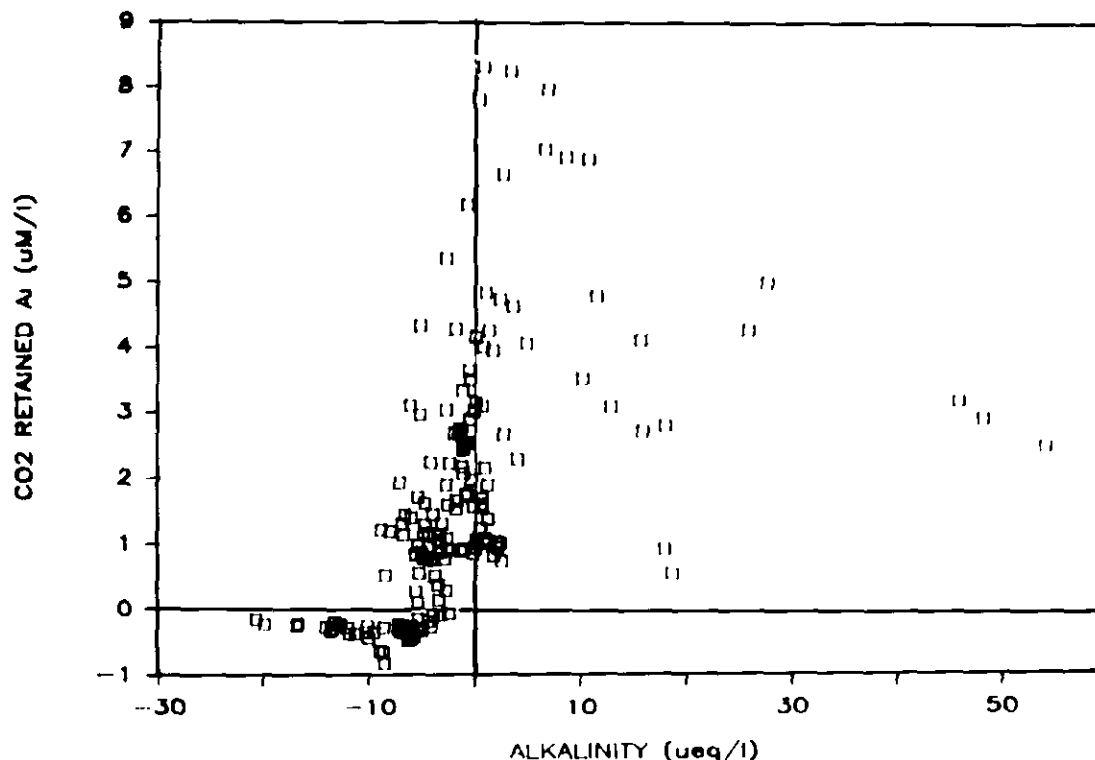| Period	Al flux, mmole/m²-day		
	Influx	Efflux	Retention
Annual average (10/1981–10/1982)	2.5	2.4	0.3
Spring high flow (3/28–6/28/1982)	5.2	5.2	−0.1
Summer base flow (7/28–10/29/1982)	1.2	0.9	0.4

FIGURE 8.   Carbon dioxide retained Al as a function of the acid neutralizing capacity of Darts Lake water. Carbon dioxide retained Al is defined as that quantity of Al held in solution by CO_2 that is oversaturated with respect to the solubility of atmospheric CO_2 assuming that the solubility of Al is controlled by the dissolution/precipitation of microcrystalline gibbsite.

reiterating the importance of Al as a buffer in dilute acidic waters, she also evaluated the role of natural organic acids. Natural organic matter reduced the degree to which Al hydrolyzed in the pH range 5.0 to 5.5, presumably due to complexation reactions, and therefore decreased the buffering of Al. Natural organic matter also participated in proton donor/acceptor reactions; the extent to which total organic carbon (TOC) would dissociate/associate protons was 0.09 eq/mole organic carbon. Johannessen (52) concluded that organic carbon was the most important weak acid/base system in acidic Norwegian waters because of the high organic carbon concentration relative to Al.

Glover and Webb (53) evaluated the acid/base chemistry of surface waters in the Tovdal region of southern Norway. The BNC of H^+ was small compared to the BNC of weak acid systems. These investigators suggested that of the total weak acid BNC, 40–60 μeq/L could be attributed to dissolved Al and Si, while 20–50 μeq/L could be attributed to natural organic acids. Solution titrations were characterized as having a major proton dissociation constant (K_a) of 10^{-6} to 5×10^{-7}, in addition to some less well defined ionization at higher pH values.

In a comparable study, Henriksen and Seip (54) evaluated the strong and weak acid content of surface waters in southern Norway and southwestern Scotland. In addition to a titrametric analysis, the Al, Si, and TOC content of water samples were determined. Weak acid concentrations, determined by Gran (55) calcula-

tion, were evaluated by multiple regression analysis. Most of the variance in the weak acid concentration could be explained by the Al and TOC content of the waters. Thus, it was concluded that the weak acid content of acidic lakes in southern Norway and Scotland was largely a mixture of Al and natural organic acids.

Driscoll and Bisogni (56) quantitatively evaluated weak acid/base systems buffering dilute acidic waters in the Adirondack region of New York State. Natural organic acids were fit to a monoprotic proton dissociation constant model (pK_a = 4.4), and the total, organic carbon proton dissociation/association sites were observed to be empirically correlated to TOC concentration. Aquo-aluminum activity, calculated from field observations, appeared to fit an $Al(OH)_3$ solubility model (Fig. 5). Calculated buffering capacity (β) is plotted as a function of pH in Figure 9 for a hypothetical system that has some properties in common with Adirondack waters (56). Buffering capacity is defined as the quantity of strong acid or base (mole/L) which would be required to change the pH of a liter of solution by one unit. Aluminum species may dominate the buffer system at low pH if these conditions are fulfilled, suggesting that the lower limit of pH observed in acidic waters with elevated Al concentrations may be controlled by the dissolution of Al. At higher pH values the buffering is regulated by the dissociation of inorganic carbon.

It is noteworthy that polymeric aluminum cations and particulate species, that may occur in acidic solutions, provide some solution buffering. However, these large
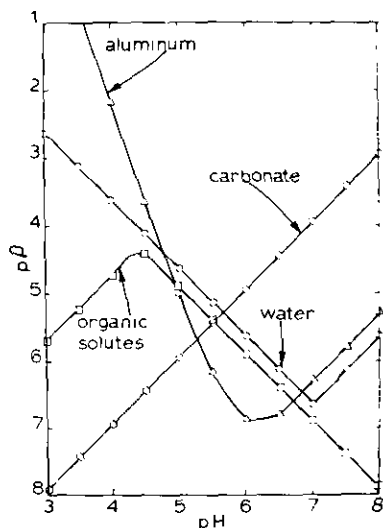
FIGURE 9. Buffer intensity diagram for dilute Adirondack water systems (56). Equilibrium with $Al(OH)_3$ (p^*K_{so} = 8.49), organic solutes (C_T = 2 × 10^{-5} mole/L; pK_a = 4.4) and atmospheric CO_2 (P_{CO_2} = $10^{-3.5}$ atm) was assumed.

units may be slow to equilibrate with the added titrant. Therefore, acid–neutralizing capacity (ANC) and BNC determinations have limitations in acidic waters due to heterogeneity phase problems.

Altering Element Cycling Within Acidic Waters

At certain times of the year and in certain regions within a watershed, acidic solutions may become oversaturated with respect of the solubility of readily forming Al minerals (Figs. 5 and 7). As discussed previously, the processes generally responsible for this condition are reduction of NO_3^- and degassing of CO_2. During conditions of oversaturation, Al will hydrolyze, forming particulate Al oxyhydroxide. The acid-soluble Al fraction mentioned earlier would include the microcrystalline hydroxide particles and their polymeric hydroxycation precursors. Smith and Hem (57) observed that during the polymerization process, Al hydroxide units displayed metastable ionic solute behavior until they contain from 100 to 400 Al atoms. When particles developed to that size their behavior was characteristic of a suspended colloid. Microcrystalline precipitate organic and inorganic solutes. The cycling or orthophosphate (13), trace metals (58,59) and dissolved organic carbon (DOC) (13,60–63) within acidic surface waters may be altered by adsorption of Al oxyhydroxides. However, few studies have addressed this specific hypothesis.

Huang (64) studied the adsorption of orthophosphate on γ-Al_2O_3. He observed an adsorption maximum at pH 4.5. While Huang (64) evaluated the adsorption of high concentrations of orthophosphate (100–1000 μmole/L), his observations of orthophosphate–Al interactions may be generally applicable to dilute surface waters.

Dickson (13) observed that when acidic lake water,

elevated in Al, was amended with orthophosphate (1.6 and 3.2 μmole/L), dissolved P was removed from solution. The removal of P was most pronounced at pH 5.5. Dickson (13,65) suggested that aqueous Al may substantially alter P cycling within acidic surface waters through adsorption or precipitation reactions. This hypothesis is noteworthy because P is often the nutrient limiting algal growth in dilute surface waters (66). Any decrease in aqueous P induced by adsorption of Al oxyhydroxides may result in a decrease in the net production of aquatic plants and an accompanied decrease in ANC generated by aquatic plants. Any decrease in ANC inputs would result in an aquatic ecosystem more susceptible to further acidification.

Aluminum forms strong complexes with natural organic matter (19). Complexation substantially alters the character of natural organic acids. Driscoll et al. (62) observed that DOC was removed from the water column of an acidic lake after $CaCO_3$ addition. They hypothesized that DOC sorbed to the particulate Al that had formed within the water column shortly after base addition. Driscoll and Schafran (48) observed decreases in water column DOC during conditions of oversaturation with respect to the solubility of $Al(OH)_3$ in an acidic lake. They hypothesized that natural organic carbon was scavenged from solution by particulate Al formed in the water column. Davis (60) has studied the adsorption of natural dissolved organic matter at the γ-Al_2O_3/water interface. He observed that natural organic matter adsorbs by complex formation between the surface hydroxyl groups of alumina and acidic functional groups of organic matter. Davis (60) indicated that DOC adsorption was maximum at pH 5. Davis and Gloor (62) reported that DOC associated with molecular weight fractions greater than 1000 formed strong complexes with the alumina surface, but low molecular weight fractions were weakly adsorbed. Davis (60) suggests that under conditions typical for natural waters almost complete surface coverage by adsorbed organic matter can be anticipated for alumina. Organic coatings may be important with respect to subsequent adsorption of trace metals and anions.

Hall et al. (63) observed a decrease in the DOC concentration of a third-order stream in New Hampshire after $AlCl_3$ addition. Moreover, a reduction in surface tension occurred at the air-stream interface and was attributed to a decrease in the solubility of DOC due to interactions with Al.

The loss of DOC in acidic waters is significant in several respects. Dissolved organic carbon represents a weak base that serves to buffer solutions against decreases in pH (52,56) (Fig. 9). In an oligotrophic acidic lake, DOC may be the constituent primarily responsible for the attenuation of light. Effler et al. (67) reported that temporal variations in the DOC of an acidic Adirondack lake accounted for much of the change in downwelling attenuation of light (K_d = -1.2 + 0.00063 DOC, where K_d is the downwelling attenuation of light/m and DOC is in μmole C/L, r^2 = 0.86, $p < 0.01$). Moreover these authors observed that variations in

DOC within the photic zone were correlated with Al concentration (Al = $-15.8 + 0.094$ DOC, where Al and DOC are in μmole/L, $n = 29$, $r^2 = 0.45$, $p < 0.0001$). They suggested that transformations in Al facilitated the removal of DOC from the photic zone (by sorption, precipitation or coagulation processes) and increased the clarity of the lake through the summer season. Decreases in the attenuation of light may enhance hypolimnitic heating while decreasing the thermal stability of lakes. Changes in the heating of lakes may potentially affect organism activity, rates of chemical reactions, vertical transport and nutrient cycling.

White and Driscoll (59) reported that the vertical deposition of Pb was strongly correlated with Al deposition in an acidic Adirondack lake. These researchers hypothesized that in-lake formation of particulate Al enhanced the vertical deposition of Pb through sorption reactions followed by sedimentation of the particulate matter. This process would appear to have implications for trace metal cycling as well as the interpretation of patterns of Pb deposition in the sediments of acidic lakes.

Aluminum Toxicity

Aluminum appears to be toxic to fish at concentrations above the range 4–8 μmole/L (44,68,69) which is at concentrations often reported for acidic surface waters. Schofield and Trojnar (44) evaluated the effects of twelve water quality parameters on the survival of stocked brook trout in Adirondack Lakes, and observed that Al was the primary factor controlling survival.

The extent of toxicity appears to be dependent on the form of aqueous Al. Baker and Schofield (68) and Driscoll et al. (25) reported that Al toxicity to fry was greatly reduced when Al was complexed to organic matter. Also survival of brook trout and white sucker fry in acidic Adirondack waters was correlated with labile monomeric Al concentrations and pH. The toxicity of Al varies with the life history stage of fish. In acidic solutions (pH 4.2–4.8), the presence of Al improved egg survival, however it resulted in reduced survival and growth of white sucker and brook trout sac fry and fry (68). Henriksen et al. (59) have reported that episodic changes in pH and labile monomeric Al during snowmelt were responsible for a fish kill of Atlantic salmon in Norway.

The mechanism of Al toxicity to fish has been attributed to the inability of fish to maintain their osmoregulatory balance and respiratory problems associated with the coagulation of mucous on the gills. Muniz and Leivestad (69) reported the loss of Na and Cl from the blood of brown trout in solutions containing 7 μmole/L Al at pH values of 5.0. Schofield and Trojnar (44) observed gill damage to brook trout at Al concentrations of 18–36 μmole/L in acidic solutions. Baker and Schofield (65) indicated that Al toxicity is most acute in solutions that are oversaturated with respect to the solubility of readily forming mineral phases.

There is very little information in the literature on the toxicity of Al to organisms other than fish in low ionic strength waters. Hall et al. (63) reported that increased rates of invertebrate drift followed Al addition to a New Hampshire stream. The drift rate of aquatic immature insects generally increased with increasing concentration of added Al, suggesting a stress-avoidance response that was a function of Al concentration. The authors also noted an increase in the drift rate of hyponeustic organisms immediately following Al addition. This response was attributed to a decrease in the surface tension of the Al-treated portion of the stream.

Conclusions

Aluminum may be transported with HCO_3^-, organic, and acidic counteranions from soil to surface waters. Within the aqueous environment Al can exhibit a variety of dissolved and particulate forms. Elevated concentrations of Al can affect the pH buffering and element transport in aquatic ecosystems, and may be toxic to aquatic organisms. Although our understanding of the chemistry and effects of aqueous Al has increased in recent years, additional research is needed to identify the source of mobile Al and mechanisms of transport from soil to surface waters, to assess the effects of Al on P, trace metal, and organic carbon cycling and to evaluate the response of aquatic organisms to various forms of Al.

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